

Electrochemical recycling of cobalt from spent cathodes of lithium-ion batteries: its application as supercapacitor

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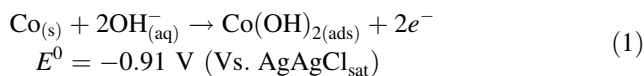
Received: 29 February 2012 / Accepted: 15 April 2012 / Published online: 28 April 2012
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Abstract The supercapacitive behavior of the metallic cobalt recycled from Li-ion batteries has been studied in this work. The reversibility of both redox process ($\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$) and ($\text{Co}^{\text{III}}/\text{Co}^{\text{IV}}$) in KOH 6 mol L^{-1} is very high and promising for capacitive applications in electrochemical devices. The specific capacitances calculated from cyclic voltammetry and electrochemical impedance spectroscopy show a good agreement, giving the value of 625 Fg^{-1} . The electrode morphology presents a high porosity, thus an electrical equivalent circuit composed of two parallel resistance and capacitance elements in series was proposed. The specific capacitance values calculated from charge/discharge curves at 0.23 and 2.3 mA/cm^2 are 601 and 384 Fg^{-1} , respectively. Thereby, it was observed that metallic cobalt recycled from ion-Li batteries is compatible with other supercapacitive materials. This shows that cobalt recycling from Li-ion batteries is economically and environmentally viable for application in supercapacitor devices.

Keywords Li-ion batteries · Supercapacitors · Cobalt recycling

1 Introduction

The supercapacitors are also known as electrochemical capacitors due their charge and discharge process to involve Faradaic reactions [1–5]. In many cases, the charge stored in supercapacitors may be greater than that in double-layer conventional capacitors [1–5]. The literature survey of supercapacitors shows that a variety of metal oxide thin films have been employed [3–7]. In these oxides, a transition metal ion with multiple valence and strong bonding power is necessary [8]. It has been focused [5–12] on the base metals (e.g., Fe, Mn, Ni, and Co) or base metal oxides (e.g., Fe_3O_4 , MnO_2 , NiO , and Co_3O_4) to decrease costs. In recent years, many efforts have been done for the development of new supercapacitors in alkaline media [1–12]. In many papers, $\text{Co}(\text{OH})_2$ is related as supercapacitor in alkaline solution of b [5–12]. Kandalkar et al. [13] described the use of $\text{Co}(\text{OH})_2$ obtained by electrodeposition of cobalt nitrate. However, few papers described the use of cobalt directly in alkaline solution. The great advantage of the utilization of metallic cobalt is the simplicity of forming a $\text{Co}(\text{OH})_2$ layer onto the electrode surface, and the cobalt electrodeposition can be a low cost [13] technique. The formation of $\text{Co}(\text{OH})_2$ onto metallic cobalt in alkaline solution is described by Eq. 1 [13].



The other advantage of this method is the possibility of cobalt recycling from Li-ion batteries. Many papers describe the cobalt recycling from spent Li-ion batteries as a valuable and environmentally friendly method [14–16]. This is because about 5.0–15 % of Li-ion cathode is composed of cobalt, and the cobalt quotation rose from US\$ 20 to US\$ 80 per kilogram

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between the years 1998 and 2010 [6]. Moreover, very pure cobalt can be obtained by acidic dissolution of lithium cobalt oxide (LiCoO_2) present in spent Li-ion battery cathode [14]. In this scenery, it is necessary to recycle the positive electrode of these batteries. This recycling of LiCoO_2 is important both economically and environmentally [14–16]. In this article, the direct application of recycled metallic cobalt as a supercapacitor in alkaline medium (KOH 6 mol L^{-1}) will be studied. The cobalt used in this study was obtained through the recycling of Li-ion cell phone batteries. The electrochemical characterization of this new material was accomplished through voltammetry, electrochemical impedance spectroscopy and charge–discharge cycles under stationary current.

2 Experimental

The cobalt bath used to obtain electrodeposition is illustrated in the Fig. 1. More details about this process can be obtained from our previous articles [14–16]. The cobalt electrodeposition was performed onto Pt inert substrate. After electrodeposition, it was applied a mechanical tension on the Pt/Co electrode to remove the metallic cobalt film. The dimensions of recycled cobalt electrode were 0.5 cm^2 of area with thickness equal to $10 \text{ }\mu\text{m}$.

Electrochemical measurements were made by means of an AUTOLAB PGSTAT power supply. The auxiliary electrode, with an area of 3.75 cm^2 , was made of platinum. A saturated Ag/AgCl was used as reference electrode. The electrochemical measurements were performed without solution agitation, at $25 \text{ }^\circ\text{C}$.

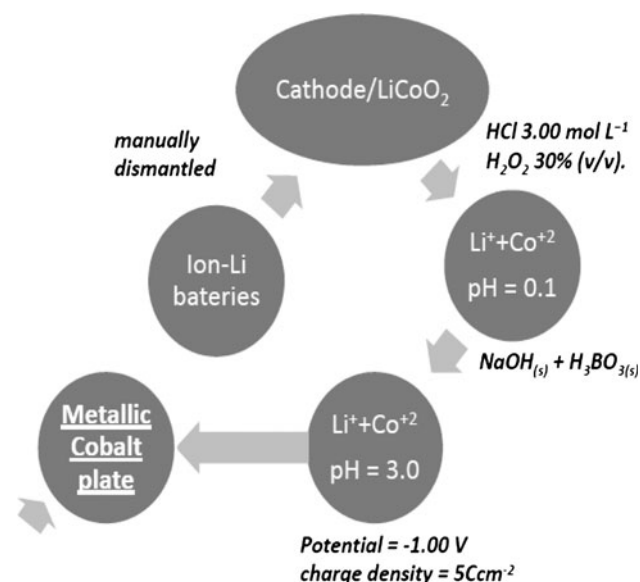


Fig. 1 Diagram showing the main steps in the recycling of metallic cobalt present in Li-ion batteries

3 Results and discussion

3.1 Potentiodynamic analysis

Initially, we performed a morphology study, measured by scanning electron microscopy (SEM), and chemical composition, measured by energy dispersive of X-ray (EDX), for recycled cobalt. In Fig. 2a, it is observed that recycled cobalt has a high porosity. From EDX, only the cobalt peaks are noted. This demonstrates the high purity of recycled cobalt. In the Fig. 2b the SEM for pure cobalt used for comparison is showed. The pure cobalt has a very low porosity compared with our recycled cobalt.

The electrochemical behaviors of recycled cobalt and pure cobalt electrodes were performed with slow scan rate (1 mVs^{-1}) linear voltammetry (Fig. 3) in KOH 6 mol L^{-1} solution between -1.2 and 0.25 V . Analogous with the behavior of Ni [13], the anodic peak in -0.89 V (Fig. 3) could be assigned to dissolution of cobalt and formation of Co(OH)_2 [5–8] (Eq. 1). The charge density for electrochemical dissolution of recycled cobalt is 0.55 C and for pure cobalt is only 0.31 C . This can be explained by the higher area obtained from process of cobalt electrodeposition. Thus, the cobalt, obtained by recycling, really has a larger area compared to pure cobalt.

Based on dissolution charge of 0.55 C , for recycled cobalt, it was calculated the expected Co(OH)_2 mass (m) using the Faraday law [8] (Eq. 2) where MM is the molar mass of Co(OH)_2 , nF is the Faraday constant ($95,500 \text{ C mol}^{-1}$) multiplied by the electrons moles involved, and i is the density current. The expected mass calculated ($370 \text{ }\mu\text{g}$) is approximately the experimental mass weight that was $410 \text{ }\mu\text{g}$.

$$m = \left(\frac{\text{MM}}{nF} \right) \int_0^t i dt \quad (2)$$

To evaluate the electrochemical behavior of recycled cobalt electrode, the cyclic voltammetry in KOH 6 mol L^{-1} solution with vertices potentials equals to -1.2 and 0.60 V (Fig. 3) was performed. The scan rate chosen was 50 mVs^{-1} because this high scan rate can increase the capacitive behavior of electrode and facilitate the reversibility calculation. In the details of Fig. 3, the pair redox A_1/C_1 is associated with the adsorption of OH^- and oxidation of Co^{II} to Co^{III} (Eq. 3), and the pair redox A_2/C_2 is associated with the adsorption of OH^- and oxidation of Co^{III} to Co^{IV} (Eq. 4) [5, 12, 14, 16]. The X-ray diffraction is shown in the details of Fig. 3.

To estimate the reversibility of the redox couples involved in the cyclic voltammetry for recycled cobalt in KOH 6 mol L^{-1} , was used the relation: $|i_a/i_c| \leq 1$, where i_a is the anodic current and i_c is the cathodic current. The

Fig. 2 The SEM and EDX for recycled cobalt (a). The SEM for pure cobalt used for comparison (b)

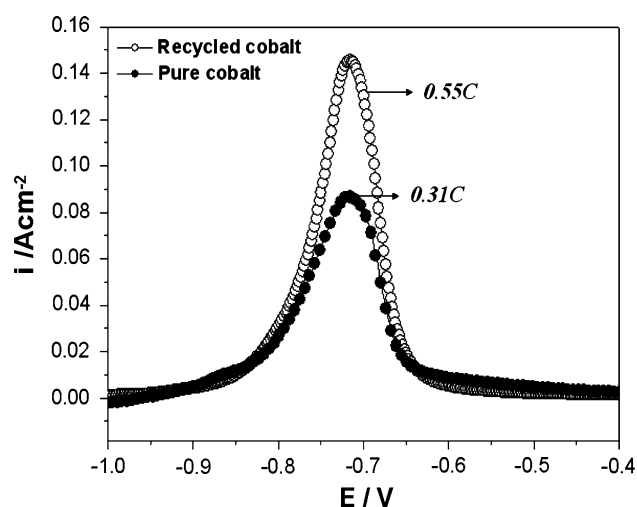
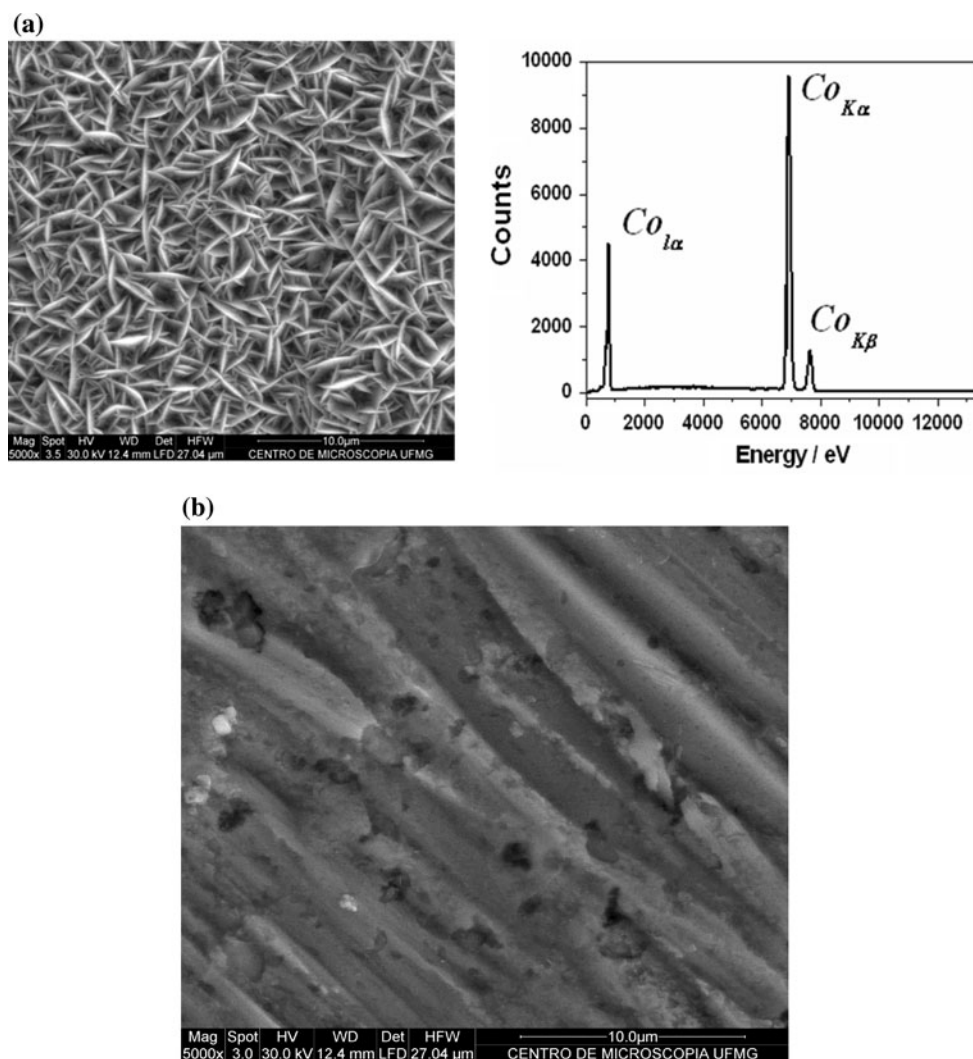
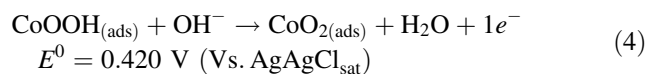
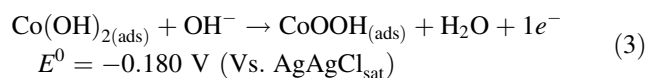


Fig. 3 Dissolution of recycled metallic cobalt in KOH 6 mol L⁻¹. The scan rate was 1 m Vs⁻¹

closer of unity the value of $|i_a/i_c|$, the redox reaction is more reversible. The reversibility of both redox processes is very high and promising for capacitive applications in electrochemical devices as shows in detail of Fig. 4.



The capacitance behavior of recycled cobalt electrode was evaluated by means of cyclic voltammetry at various sweep-rates (dE/dt or s). Differential capacitance (C) data were derived as a function of potential from recorded voltammetric response currents, i , given by Eq. 5 [5, 7, 10]:

$$i = C \left(\frac{dE}{dt} \right)_{[\text{OH}^-], \text{T}, \text{P}} \quad \text{or} \quad i = Cs \quad (5)$$

The cyclic voltammetry responses of recycled cobalt electrode in 6.0 M KOH are shown in Fig. 5. The potential

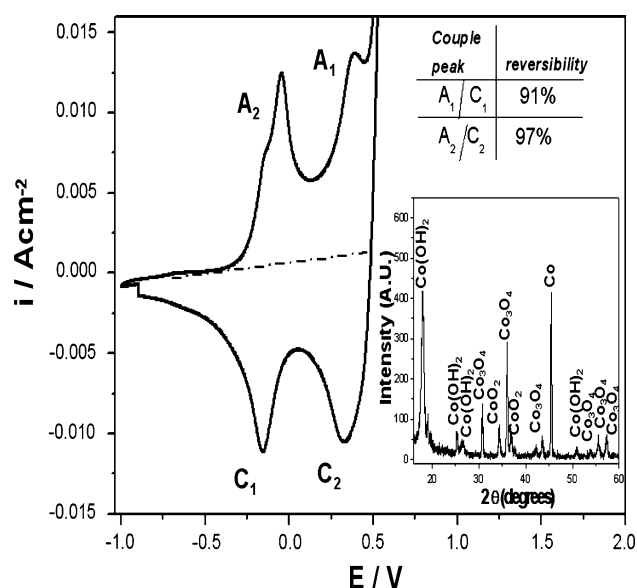


Fig. 4 The cyclic voltammetry of recycled metallic cobalt in KOH 6 mol L⁻¹ with scan rate of 50 m Vs⁻¹. In detail is shown the X-ray diffraction of electrode after cyclic voltammetry

window is widened from -1.00 to 0.60 V versus saturated Ag/AgCl electrode. As well, the current dependence (at 0.40 V) on the sweep rate is shown in detail of Fig. 4. The linear dependence of scan rate and current density, in this graphic, shows that the capacitance (the slope) is constant and its value is 0.25 Fcm⁻². The specific capacitance calculated was 625 Fg⁻¹. The reversibility of cobalt electrode, along with the linear current versus scan rate, confirms its capacitive nature in alkaline electrolyte in this range of potential (-1.00 to 0.6 V).

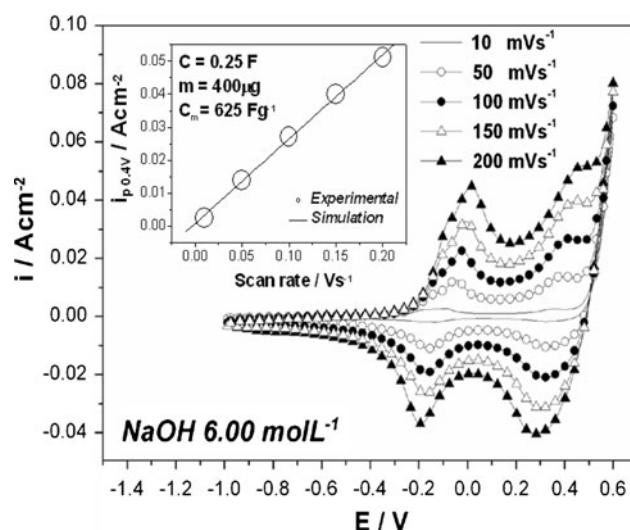


Fig. 5 The cyclic voltammetry of recycled metallic cobalt in KOH 6 mol L⁻¹ with different scan rates. In detail is shown the peak density current in 0.40 V versus scan rate

3.2 Impedance measurements

The AC-impedance measurements were carried out over the frequency range of 10⁴–10⁻² Hz at open circuit potential (OCP). The Nyquist diagram in recycled cobalt is shown in Fig. 6a. The electrode morphology is presented with a high porosity (SEM shows in Fig. 6b), thus a common electrical equivalent circuit composed of two parallels [RQ] elements in series was proposed (detail of Fig 6a). The R₁ is the solution resistance, R₂ and Q₁ are polarization resistance and non ideal capacitance of double layer respectively. The R₃ and Q₂ are pores resistance and non ideal capacitance into the pores respectively. Values of the circuit elements analyzed are shown in Table 1. The sum of non-ideal capacitances (Q₁ and Q₂) is equal to 0.27 Fcm⁻². This value is similar to that obtained by cyclic voltammetry showing the consistency of the two electrochemical techniques.

3.3 Charge/discharge analysis

The charge/discharge electrochemical behavior of recycled cobalt electrode was performed by galvanostatic method at

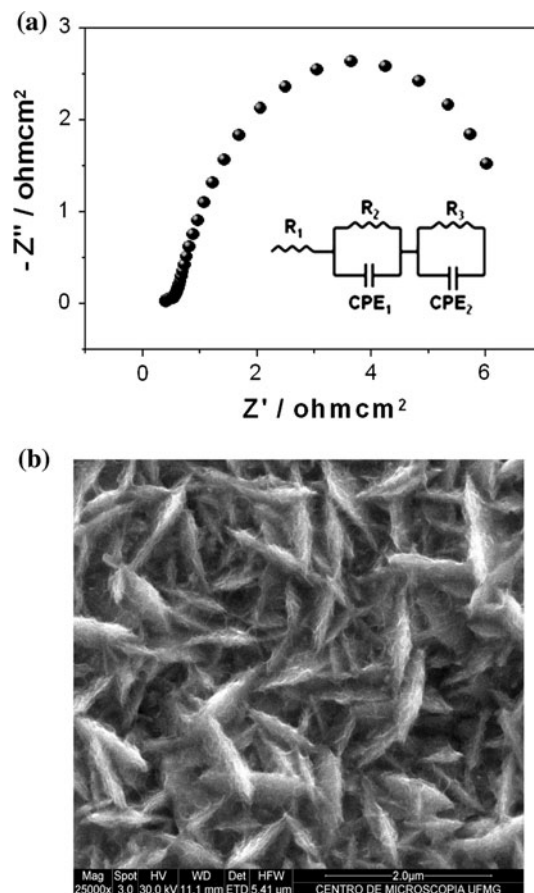


Fig. 6 The Nyquist diagrams for metallic cobalt in KOH 6 mol L⁻¹ at OCP. In detail an electrical equivalent circuit proposed (a). The SEM of the electrode for metallic cobalt with magnification ×25,000 (b)

Table 1 Values of the circuit elements in AC-impedance measurements of recycled metallic cobalt in KOH 6 mol L⁻¹

Element	Values
R ₁	0.26 Ohm cm ²
R ₂	0.44 Ohm cm ²
Q ₁ Y ⁰	0.11 Fcm ⁻²
R ₃	5.03 Ohm cm ²
Q ₂ Y ⁰	0.91 Fcm ⁻²

constant currents of 0.23 and 2.3 mA/cm² between -1.00 and 0.4 V. Figure 6 shows typical charge–discharge curves at 0.23 and 2.3 mA/cm². Their specific capacitance can be calculated according to the Eq. 6 [5, 14, 18] where C_m (Fg⁻¹) is the specific capacitance, I (A) is charge/discharge current, Δt (s) is the discharging time, ΔE represents the potential drop during discharge process and m (g) is the mass of Co(OH)₂ (410 µg). The specific capacitance values calculated from the discharging curves at 0.23 and 2.3 mA/cm² are 601 and 384 Fg⁻¹ respectively.

$$C_m = \frac{I(\Delta t)}{(\Delta E)m} \quad (6)$$

The specific capacitances at both current densities are all larger than those of the other supercapacitor electrodes reported [2, 4, 5, 18].

The electrical parameters, specific energy (E) and specific power (P) are calculated using the Eqs. 7 and 8 respectively. In these equations I_d and t_d are the discharge current and discharge time, respectively and m corresponds to experimental mass of Co(OH)₂ (410 µg). In a similar study, Kandalkar et al. [13] presented specific capacity and specific energy equals to 165 Fg⁻¹ and 6.5 W h Kg⁻¹ respectively. Other authors have specific values of capacitance and specific energy as shown in Table 2.

According to Fig. 7, it is observed that our values for the specific capacity and specific energy are 601 Fg⁻¹ and 27.71 W h Kg⁻¹ respectively. Thereby it is observed that the recycled metallic cobalt behaves compatibly with other similar materials [19]. This shows that the recycling of cobalt is economically and environmentally viable.

$$E = \frac{0.8I_d t_d}{m} \quad (7)$$

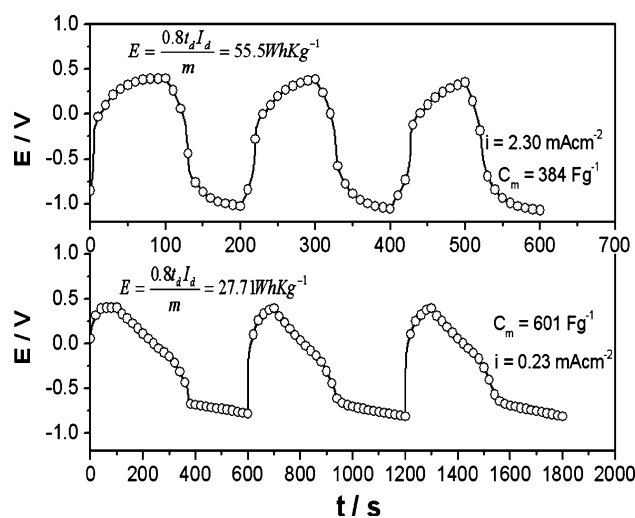
$$P = \frac{0.8I_d}{m} \quad (8)$$

4 Conclusion

The supercapacitive behavior of the metallic cobalt recycled from Li-ion batteries has been studied in this work. The reversibility of both redox process (Co^{II}/Co^{III}) and

Table 2 Values of specific capacity and specific energy obtained from other authors

References	Especific capacitance/ Fg ⁻¹	Especific energy W h kg ⁻¹	Material	Electrolyte
[17]	326.4	13.2	CoS	KOH 1 mol L ⁻¹
[2]	263–418	–	Co ₃ O ₄ / nanotube	KOH 2 mol L ⁻¹
[1]	574	–	Co ₃ O ₄ / nanotube	KOH 6 mol L ⁻¹
[18]	720	–	RuO ₂	KOH 6 mol L ⁻¹
[4]	630	–	CoMnO ₂	KOH 1 mol L ⁻¹

**Fig. 7** Charge and discharge current for metallic cobalt in KOH 6 mol L⁻¹ with current density equal to 0.23 and 2.3 mA/cm²

(Co^{III}/Co^{IV}) in KOH 6 mol L⁻¹ is very high and promising for capacitive applications in electrochemical devices. The specific capacitances calculated from cyclic voltammetry and electrochemical impedance spectroscopy show a good agreement with the value of 625 Fg⁻¹. The electrode morphology presents a high porosity, thus an electrical equivalent circuit composed by two parallels [RC] elements in series was proposed. The specific capacitance values calculated from the discharge curves at 0.23 and 2.3 mA/cm² are 601 and 384 Fg⁻¹ respectively. Thereby it was observed that metallic cobalt recycled from ion-Li batteries is compatible with other supercapacitive materials. This shows that the recycling of cobalt is economically and environmentally viable.

Acknowledgments The authors acknowledge UFMG, CNPq, FAPEMIG and CEMIG for financial support.

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